NANOSTRUCTURE FABRICATION USING MICROBIAL MANDREL

TECHNICAL FIELD

This invention relates generally to fabrication processes for nanostructures and more particularly to use of microbial mandrels in fabrication of nano-tube structures.

BACKGROUND

Many applications have been identified for nanostructures. In many of these applications, such as polymer reinforcements, electrodes for batteries and fuel cells, electron-emitters, gas filters, etc., the arrangement of the nanostructures can be a random or nearly random collection of hundreds, thousands, or millions of nanostructures. Some of the fabrication methods for nanostructures are well suited for fabricating the structures in such random positions and orientations. Some applications can use individual nanostructures that can be manipulated into particular configurations by using microscopic manipulation tools such as MEMS tweezers, laser light tweezers, etc. However, many other applications require orderly arrangements of nanostructures in arrays, which is not always easy to achieve.

BRIEF DESCRIPTION OF THE DRAWINGS

The features and advantages of the disclosure will readily be appreciated by persons skilled in the art from the following detailed description when read in conjunction with the drawings, wherein:

FIGS. 1, 2, 3A, 4A, and 5A are perspective views of various stages in an embodiment of a fabrication method performed in accordance with the invention.

FIGS. 3B, 4B, and 5B are side elevation cross-section views of structures corresponding to FIGS. 3A, 4A, and 5A respectively.

FIG. 6 is a flow chart illustrating an embodiment of a fabrication method performed in accordance with the invention.

DETAILED DESCRIPTION OF EMBODIMENTS

Throughout this specification and the appended claims, the prefix “nano-“ and the terms “nano-scale,” “nanostructure,” “nano-tube,” etc. denote structures having minimum dimensions of the order of about a micrometer or less. Maximum dimensions, such as the length of a rod or tube, may of course be larger. The term “propagule,” in addition to its ordinary reproductive meaning synonymous with “disseminule,” denotes any precursor form of a nano-scale biological structure. For simplicity and clarity of the exposition, all the embodiments described below refer to nano-scale biological structures as “microbes” and use the adjective form “microbial.”

In accordance with one aspect of the present invention, a method is provided for fabricating nano-scale structures by using microbes as mandrels for forming nanostructures. One embodiment of such a method includes providing a substrate, depositing a nutrient medium on the surface of the substrate, introducing microbes or propagules thereof onto the nutrient medium, growing the microbes to form elongated oriented sacrificial mandrels, coating each oriented sacrificial mandrel with an outer layer of a desired nano-tube material, and removing the sacrificial mandrels, while leaving oriented nano-tubes.

FIGS. 1, 2, 3A, 4A, and 5A are perspective views of various stages in such an embodiment of a fabrication method performed in accordance with the invention, and FIG. 6 is a flow chart illustrating the method embodiment. In FIG. 6, various steps of the method are denoted by reference numerals **S10**, **S20**, . . . , **S90**.

For high yield and quality, the method is performed in an environment that is substantially free of undesired organisms. This can be achieved by providing an environment that is initially sterile (step **S10**). The fabrication uses a substrate **10** on which microbes will not grow (step **S20**). Substrate **10** can be a clean, bare, planar surface of metal, semiconductor, or insulator, for example. A silicon wafer, similar to those used in semiconductor integrated circuit fabrication processes, is a convenient kind of substrate. Glass and quartz substrates are also convenient alternatives. As shown in FIG. 1, a quantity of nutrient material **20** is deposited (step **S30**) on substrate **10** and optionally patterned (step **S35**), and a suitable microbe propagule **30** is introduced on the patterned nutrient (step **S40**). Any propagules introduced onto parts of the substrate that are free of nutrient will not grow.

Optionally, in applying the method to make a number of nanostructures simultaneously, selected propagules **30** may be irradiated (step **S45**) with actinic radiation such as ultraviolet light or X-rays to prevent their growth. Irradiating step **S45** may be used as an alternative to, or in addition to, patterning step **S35** in some applications of the method. The pattern formed by the patterned nutrient has dimensions commensurate with the desired size and orientation of the microbe to be grown.

In the next part of this method embodiment, a sacrificial mandrel is formed (step **S50**). On the nutrient, a microbe **40** grows from the propagule (step **S60**), generally following the pattern of the nutrient, as shown in FIG. 2. Optionally, a portion of the nutrient may be removed (step **S65**) by conventional masking and non-directional etching techniques if needed to provide an opening **45** under microbe **40** (FIG. 3A). Microbe **40** is optionally conformally coated with a

polymer layer **50**, as shown in FIGS. 3A and 3B (step **S70**). This forms a sacrificial mandrel for the succeeding steps.

FIGS. 3B, 4B, and 5B are side elevation cross-section views of structures corresponding to FIGS. 3A, 4A, and 5A respectively. In FIG. 3B, the core of the sacrificial mandrel is the microbe **40**, and the outer layer consists of conformal polymer coating **50**. Polymer layer **50** may be polymethylmethacrylate (PMMA), a polyimide, or a photoresist, for example, though generally photosensitivity is not required. Polymer layer **50** may conveniently be polymerized *in situ* on the microbe surface, for example with parylene, which readily forms a conformal coating when polymerized *in situ*. Another useful alternative polymer for polymer layer **50** is a polynorbornene, such as Unity™ Sacrificial Polymer, which may be cleanly removed by pyrolysis at 350-425 C. This material is commercially available from Promerus Electronic Materials of Brecksville, OH. Polymer layer **50**, if used, serves to stiffen the sacrificial mandrel and to prevent collapse. The sacrificial mandrel is coated with a layer of material **60** chosen to form the desired nanostructure (step **S80**).

Outer layer material **60** may be an inorganic substance, a conductive material such as a metal, a semiconductor, or an insulator as appropriate to the application. Gold is a suitable metal for many applications. Many suitable materials are known to those skilled in the art, including the conventional materials used in semiconductor integrated circuit fabrication.

While FIGS. 3A, 3B, 4A, and 4B show intermediate polymer layer **50**, the microbe itself may be used as the sacrificial mandrel, without intermediate layer of polymer **50**. That is, the nanostructure material **60** may be conformally coated directly onto microbe **40**.

In step **S90**, the sacrificial mandrel is removed, leaving nanostructure **70**. FIG. 5B illustrates the cross-section of the hollow nanotube formed in this example. Any remaining nutrient material **20** can be removed from the substrate at the same time, e.g., by the same process by which the sacrificial mandrel is removed. Step **S90** of removing the sacrificial mandrels may be performed in vacuum or partial vacuum, e.g. by plasma etching with oxygen

plasma. Alternatively, step **S90** of removing the sacrificial mandrels may be performed by wet etching, e.g., with nitric acid.

It will be understood that non-pathogenic microbes should be used. While the elongated microbes **40** shown in the drawings have a generally cylindrical rod shape, those skilled in the art will recognize that other forms of microbes exist that can be used in the methods of the present invention. Various shapes, such as coccus, rod, spiral, and helical prokaryotes are suitable. Some eukaryotic microbes, such as animals, plants, and fungi, are also suitable, as noted hereinbelow.

Other microbial shapes of microbe **40** that may be chosen for particular applications include globose, subglobose, oblate spheroidal, suboblate spheroidal, ellipsoidal, oval, fusiform, filiform, acerose, discoidal, lenticular, bacilliform, sigmoid, reniform, allantoid, lunate or crescentic, falcate, ovoid, obovoid, lecythiform, pyriform, obpyriform, clavate, obclavate, capitate, spathulate, bicampanulate, turbinate, rhomboidal, cuneiform, dolabriform, campanulate, napiform, biconic, lageniform, peltate, ampulliform, doliiform, cymbiform or navicular, acicular, subulate, hamate or uncinate, corniform, circinate, and ventricose shapes, and shapes with papillate, mucronate, or acute apices.

Some specific suitable microbes are filamentous fungi, exemplified by the genera Acremonium, Fusarium, and Penicillium; filamentous bacteria, including Cyanobacteria and Actinomycetes; filamentous animals, including, for example, filamentous Chromista, such as the genus Saprolegnia and allies; filamentous plants, such as the algae genera Spirogyra, Tribonema, Oedogonium; and the filamentous, silicaceous diatoms, such as the genus Melosira.

As a particular example of a useful choice for the microbe shape, helical microbes may be used as the cores of the sacrificial mandrels to make nano-springs by methods performed in accordance with the present invention.

A suitable nutrient **20** is conventional agar-agar culture medium, which may be deposited as a thin film on substrate **10** and patterned by conventional lithographic methods, including ink-jet-printing methods or embossing (imprint)

lithography. Additional conventional nutrients such as malt may be mixed with the agar-agar for particular microbes if desired. Alternatively, other conventional microbe nutrients may be used.

In employing the methods of the present invention to fabricate a nanostructure array consisting of many nanostructures, the nanostructures are made simultaneously on the same substrate **10**. At least propagule-introducing step **S40** and microbe-growing step **S60** of FIG. 6 are performed in an environment substantially free of undesired organisms and having illumination and temperature range controlled to be suitable for microbial growth. In nutrient-medium-patterning step **S35**, the nutrient is patterned to form a multiplicity of nutrient islands spaced apart from each other. This patterning may be done before step **S40** of introducing propagules **30**. If the microbes introduced onto the nutrient medium are elongated (e.g., generally cylindrical) and have a characteristic diameter, patterning of the nutrient medium in step **35** may include forming islands having at least one lateral dimension greater than or equal to the characteristic diameter of the microbes. The microbes tend to grow parallel to the direction of the longer dimension of the islands.

Thus, another aspect of the invention is an array of nano-tubes, fabricated by the methods described hereinabove. The spacing and orientations of the nanotubes of the array are determined by the spacing and orientations of the islands of nutrient previously patterned.

A specific embodiment of a method for fabricating nano-scale structures performed according to the invention includes the steps of providing a substrate **10** having a surface on which microbes cannot grow, providing an environment substantially free of undesired organisms, depositing and patterning a nutrient medium **20** on the surface of the substrate to form a multiplicity of nutrient islands spaced apart from each other, introducing elongated, generally cylindrical microbes **40** or their precursors **30** onto the nutrient medium, growing the microbes **40** to form oriented sacrificial mandrels, optionally removing a portion of the nutrient medium **20**, coating each oriented sacrificial mandrel with an intermediate layer of polymer **50** and an outer layer **60** of a desired nano-

tube material, and removing the sacrificial mandrels and the intermediate layer of polymer, while leaving oriented nano-tubes **70**. If the intermediate polymer layer **50** is not needed, it may be omitted. These embodiments of the method may also be practiced by performing the steps in the order recited above, or the order may be varied for particular applications. For example, in some instances, the nutrient medium **20** may be patterned after introducing microbes **40** or their precursors **30**.

In accordance with another aspect of the invention, an array of nanostructures is provided, comprising a multiplicity of nanostructures disposed in a predetermined pattern on a substrate, the nanostructures being oriented in a predetermined orientation, and the nanostructures being characterized by interior dimensions commensurate with the dimensions of predetermined microbes. A simple example of each nanostructure of such an array is a nano-tube.

In accordance with yet another aspect of the invention, a method is provided for using microbes **40** to form nano-tubes, the method comprising the steps of providing a substrate **10**, depositing a nutrient medium **20** on the surface of the substrate, introducing elongated microbes **40** or their precursors **30** onto the nutrient medium, growing the microbes **40** to form oriented sacrificial mandrels, optionally removing a portion of the nutrient medium **20**, coating each oriented sacrificial mandrel with an outer layer of a desired nano-tube material **60**, and removing the sacrificial mandrels, while leaving oriented nano-tubes. As described above, an intermediate polymer layer **50** may be used between microbes **40** and outer layer **60** if desired.

In accordance with another aspect of the invention, a nano-scale structure carried by a substrate may be made. Such a nano-scale structure comprises an elongated microbe, the microbe being affixed to the substrate at one of its ends; a polymer coating covering the elongated microbe; and an inorganic coating covering the polymer coating. The inorganic coating may comprise a conductor, a semiconductor, or an insulator. As described hereinabove, another nano-

scale structure may be formed by removing the microbe and/or by removing both the microbe and the polymer coating.

INDUSTRIAL APPLICABILITY

Methods of the present invention may be used to make an individual nanostructure, a few isolated nanostructures, or a regular array consisting of a number of nano-scale structures. Nanostructures made in accordance with the present invention may be used in many applications similar to those of single-wall carbon fullerene nanotubes, such as electron emitters, as well as in many other industrial applications where nano-scale elements of various shapes, such as nano-tubes or nano-springs, are needed. An integrated circuit incorporating conductive nanostructures may be made by using the methods of the invention.

Although the foregoing has been a description and illustration of specific embodiments of the invention, various modifications and changes thereto can be made by persons skilled in the art without departing from the scope and spirit of the invention as defined by the following claims. For example, the order of steps in the methods may be varied, and equivalent materials may be used other than those used in the example embodiments described. Methods performed in accordance with the invention may be repeated a number of times and combined with other steps, including conventional semiconductor fabrication methods, to fabricate more complex nanostructures.